

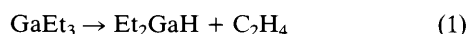
## Infrared Laser-powered Synthesis and Properties of Diethylgallane

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Diethylgallane, characterised by IR and  $^1\text{H}$  NMR spectroscopy, has been prepared by the infrared laser powered pyrolysis of triethylgallane vapour, providing the first direct observation of this species in the pyrolysis.

Dialkylgallanes,  $\text{R}_2\text{GaH}$ , have been proposed as the primary products of pyrolysis of trialkylgallanes containing  $\beta$ -hydrogens,<sup>1</sup> as exemplified in reaction (1).



This hypothesis, based on the similar behaviour of analogous trialkylalanes,<sup>2</sup> is supported by a considerable body of indirect evidence. Thus transalkylation has been observed to occur in the co-pyrolysis of tri-isobutylgallane and ethene at temperatures from 416 to 500 K,<sup>3</sup> and the simple pyrolysis of triethylgallane results in the formation of ethene and hydrogenated gallium.<sup>4</sup> However, attempts to isolate the dialkylgallane produced in reaction (1) have been frustrated by competing reactions such as the reverse reaction and catalysed polymerisation of the alkene.<sup>5</sup> Indeed, there are few unambiguous reports of free dialkylgallanes; Baxter *et al.* have recently reported the synthesis of dimethylgallane from trimethylgallane and sodium gallohydride,<sup>6</sup> Eisch<sup>5</sup> has prepared diethylgallane by the transhydrogenation of diethylchlorogallane and diethylalane, and Markova *et al.*<sup>7</sup> have used a similar method in the preparation of di-isobutylgallane. Here we show that the unique characteristics provided by infrared laser powered homogeneous pyrolysis (IR LPHP) may be utilised in a simple and straightforward synthesis of diethylgallane *via* reaction (1).

We have recently initiated an extensive programme of study into the pyrolysis of simple alkyls of main group metals, in order to elucidate the mechanisms involved.<sup>8,9</sup> In these studies, we have utilised the technique of IR LPHP, which has a number of advantages in the study of this type of reaction. Briefly, in this technique a mixture of the target gas and a photosensitiser at pressures of a few mmHg (1 mmHg = 133 N m<sup>-2</sup>) is contained in a cylindrical Pyrex cell of volume ~100 cm<sup>3</sup>. The cell is fitted with ZnSe windows, which permit the passage of IR laser radiation (~5 W) from a free-running CO<sub>2</sub> laser, and the monitoring of the cell contents by Fourier transform IR spectroscopy. As shown in more detail elsewhere,<sup>8,10</sup> this arrangement generates a static temperature profile in which the centre of the cell may reach as high as 1500 K, but in which the cell walls remain at room temperature. As far as mechanistic studies are concerned, this arrangement has a number of advantages. These include the elimination of wall initiation or loss reactions, the use of very small quantities, and an enhancement of the lifetime of unstable reaction products; the last feature arises from the rapid migration of primary products into cool regions of the cell on formation. The photosensitiser of choice is SF<sub>6</sub>, which has very strong absorption of IR radiation in the CO<sub>2</sub> laser region, very fast inter- and intra-molecular energy transfer, and a low thermal conductivity; it is also chemically inert.

Figure 1 shows the FTIR spectrum of a mixture of Et<sub>3</sub>Ga (4 torr) and SF<sub>6</sub> (10 torr), both before (A) and after (B) exposure to 5 W to CO<sub>2</sub> laser radiation for a period of 30 s. Longer exposures led to a loss of bands assignable to organogallium species, and deposition of metallic gallium. The most prominent feature of (B) is the appearance of a broad, strong absorption at 1640 cm<sup>-1</sup>; as well as other new peaks

corresponding to ethene, there are also weaker additional peaks at 1376 and 1188 cm<sup>-1</sup>, and shifts of the features in the CH stretching region (not shown in Figure 1). Taking the integrated peak area in the CH stretching region as an approximate guide, conversion to Et<sub>2</sub>GaH is almost quantitative. The IR spectrum of Et<sub>2</sub>GaH has not previously been reported, but the new features are readily ascribed to this species on comparison with the spectra of the corresponding methyl<sup>6</sup> and isobutyl<sup>17</sup> compounds, as well as analogous aluminium species.<sup>11</sup> As in the case of Me<sub>2</sub>GaH<sup>6</sup> and Me<sub>2</sub>AlH<sup>11</sup>, the vapour produced in this fashion consists of a mixture of dimers and trimers, with the latter heavily predominating in this case. These conclusions are drawn from the relative intensities and positions of the new bands, which are readily attributed to ring Ga-H stretching modes.<sup>6,7</sup> As shown by Howard *et al.*,<sup>12</sup> such an H-bridged ring system is expected to exhibit two strongly IR active Ga-H stretching modes, whose separation depends on the Ga-H-Ga bridge angle: the broad band at 1640 cm<sup>-1</sup>, and a second obscured by the strong SF<sub>6</sub> absorption near 940 cm<sup>-1</sup>, are thus attributed to a trimeric form with a bridging angle near 120°, whereas the other two arise from the dimer with an angle of approximately 98°. On gently warming the cell, all peaks ascribed to the new species increased in intensity; this fact, together with the observation of a colourless viscous condensate on the cell walls, indicates that the vapour pressure of the diethylgallane at room temperature is less than 1 torr.

Attempts to isolate this product for further analysis by condensation at 77 K pumping at 197 K (at which temperature C<sub>2</sub>H<sub>4</sub> and SF<sub>6</sub> are removed) and re-expansion into the cell<sup>8</sup> resulted only in the recovery of a reduced pressure of the Et<sub>3</sub>Ga starting material. This is in accord with the suggestion made by Eisch<sup>5</sup> that the diethylgallane product undergoes disproportionation over a period of time; an alternative explanation may be that, at the low temperatures used, the material is converted to a higher polymeric form of lower

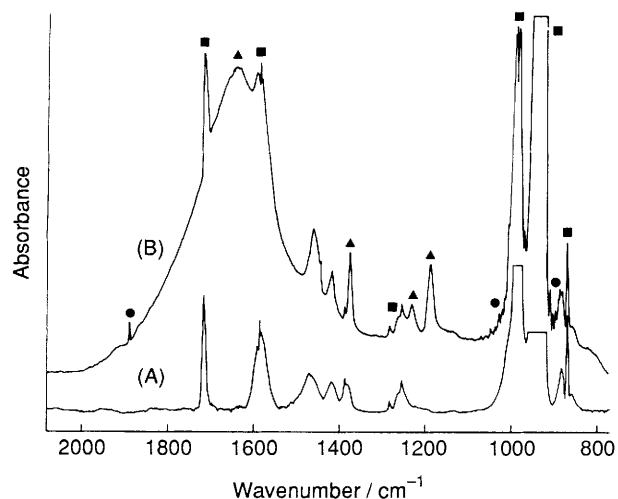


Figure 1. Fourier transform IR spectrum of SF<sub>6</sub> (10 torr) and Et<sub>3</sub>Ga (4 torr), before (A) and after (B) exposure to laser irradiation. Features marked are assigned as follows: ■ = SF<sub>6</sub>, ● = C<sub>2</sub>H<sub>4</sub>, ▲ = Et<sub>2</sub>GaH.

vapour pressure. On the other hand, the product does seem to be indefinitely stable in the vapour phase at room temperature.

It did prove possible, however, to obtain a  $^1\text{H}$  NMR spectrum of the reaction products on condensation into  $\text{C}_6\text{D}_5\text{CD}_3$ . At room temperature, a broad unresolved peak at  $\delta_{\text{H}}$  3.07 was found; this compares with the GaH resonance at  $\delta_{\text{H}}$  3.06 found for  $\text{Me}_2\text{GaH}$  in  $\text{C}_6\text{D}_5\text{CD}_3$  at  $-20^\circ\text{C}$ .<sup>6</sup> The region of CH proton resonances is complicated by overlap with those of the  $\text{Et}_3\text{Ga}$  formed in the disproportionation; although the Me protons yielded a clear 1:2:1 triplet at  $\delta_{\text{H}}$  1.21 [ $J(\text{CH}_3\text{-CH}_2)$  8.0 Hz], the  $\text{CH}_2$  protons produced a broad structured feature whose chemical shift varied, depending on the details of the condensation process, between  $\delta_{\text{H}}$  0.60 and 0.70. This latter we attribute to rapid exchange of ethyl groups between  $\text{Et}_3\text{Ga}$  and  $\text{Et}_2\text{GaH}$ , resulting in a weighted average for these protons; apparently the chemical shift of the Me protons is fairly similar in the two species. This behaviour parallels that in mixtures of  $\text{Me}_2\text{AlX}$  compounds.<sup>13</sup> On cooling, the GaH resonance underwent a pronounced narrowing and shift to lower frequency, reaching  $\delta_{\text{H}}$  2.85 at  $-36^\circ\text{C}$ . At the same temperature, the Me resonance consisted clearly of two overlapped 1:2:1 triplets centred at  $\delta_{\text{H}}$  1.29 and  $\delta_{\text{H}}$  1.23, while the  $\text{CH}_2$  resonance split into two 1:3:3:1 quartets at  $\delta_{\text{H}}$  0.76 and  $\delta_{\text{H}}$  0.38; all  $J(\text{H-H})$  remained at 8.0 Hz. On the basis of the relative intensities of the GaH and CH resonances and comparison with a pure  $\text{Et}_3\text{Ga}$  sample, we assign the higher frequency of these in each case in  $\text{Et}_2\text{GaH}$ .

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